Chemicals in the Environment

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• *Synthetic chemicals are now being incorporated into the earth's ecosystems at a rate and in such manners as to alarm environmentalists. These chemicals are the uncontrolled waste products of a technological society. Most prominent among them at the present time are organochlorine, organomercurial and lead compounds. Persistent members of these groups disperse in water, air and animal tissues. Also they have the capacity for concentration in animal food chains, thereby reversing the historical expectation of the dilution and degradation of wastes.*

Examples of damage from environmental residues to man are at this stage speculative but documentation from effects on wild species is abundant. Already several species of birds seem on their way to extinction. These wild species constitute a gratuitous monitoring system which already has signaled clear warnings for the welfare of man.

THE PRESENCE of novel chemicals in natural systems is a consequence of technological man. The appearance of such synthetic chemicals and the effects they produce have no precedent in organic evolution. Most pesticides, for example, as we know them today, have no natural chemical counterparts. Indeed most did not exist thirty years ago. Lead and organic mercury, now causing such contention, have only been recognized as serious environmental pollutants in the last decade. These and other waste products of technicized society inevitably become components of the environment. Many of these waste materials have the capacity to inflict permanent changes upon the earth's ecosystems. First, to understand these effects and, second, to control and to regulate pollutants must be the major goals of the socially responsible environmentalist.

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This presentation centers around two classes of persistent and hazardous environmental pollutants – the organochlorines and the organomercurials. I will concentrate on pesticides within these classes although not all chemical pollutants within these classes are so used. It is important to note at the outset that one may construct from chemical characteristics, and later ecological response, a model for predicting effects irrespective of the sources and the uses to which these chemicals are put.

General Characteristics of Persistent Pollutants

Persistent pollutants will share some or all of the following characteristics:

• They persist for long periods of time and, more importantly, can neither be disposed of nor, when incorporated into ecosystems, controlled. Chemical stability characterizes such compounds as p, p′DDE (a DDT derivative) which is comparatively resistant to degradation by the usual detoxification mechanisms of vertebrates, to microbial action, and to non-biological breakdown in the environment.

- Water-soluble waste products are normally diluted and not accumulated in organisms. Insoluble products such as the polychlorinated biphenyls (PCB), methyl mercury and p, p′ DDE can be concentrated in biological tissues and can be transported along food chains to reach their greatest amounts in terminal carnivores.

- Residue dispersal is favored by fluid transport, either air or water. Although vapor pressures of potential pollutants may be low, amounts entering the atmosphere could be significant over periods of time, especially when rates of vaporization are greatly increased by codistillation with water.[1] Leaching and adsorption to soil particles suspended in runoff waters often explain pesticide movement. The global distribution of DDT, for example, can only be explained by aerial dispersal with subsequent fallout, in conjunction with transport by water.

- Following dispersal of residues, differential magnification in biological systems may be expected and may cause unintended and unpredictable results.

- Large-scale production of primary pollutants is required before general ecosystemic hazard is posed. The organochlorine insecticides (DDT, dieldrin, toxaphene and others) fit this category. Annual world production of DDT has approximated a quarter billion pounds for some years. Even in the position of "phasing out," DDT use in California alone in 1969 was 2.4 million pounds. The arochlors (PCB) also meet this criterion. Their usefulness in the manufacture of many plastics, paints and resins derives in large part from their chemical stability and resistance to degradation.

- "Point" sources of pollutants such as effluents from industry are more easily regulated than are "general" sources such as agricultural lands, watersheds and contaminated air. General sources of contamination are the prime threat to ecosystems. Still, regional fallout patterns exist with highest concentrations in industrial regions.[2]

The Fact of Residual Occurrence

There is now no question that organochlorine residues occur widely over the earth. Soils, water, flora and fauna frequently show them. We continue to be surprised at the places where these residues are found—flowing waters,[3] marine ecosystems,[4] petrels over open ocean,[2,5] aerial dust over continental areas,[6] aerial dust over open ocean,[7] and fish and wildlife.[8] Indeed Peterle[9] recently suggested that as much as 2,684 tons of DDT and its degradation products may be imbedded in Antarctic snow and ice. Probably the most abundant synthetic pollutant on earth is a breakdown product of DDT, p,p′ DDE. Organic mercury has been reported widely throughout the earth. In Sweden and Japan it has produced human death and injury[10] and in many areas, notably the Great Lakes Region, above-threshold amounts (0.5 ppm) are commonly found in fishes. In August of this year the California Department of Fish and Game announced above-threshold amounts in fishes from the Delta Region and from Clear Lake.

The foregoing listing establishes only that residues of synthetic pollutants occur commonly. The list could be considerably expanded.[10-15]

Three "Case Histories"

A close look at the distributional patterns and degradation histories of three kinds of chemical residues will illustrate the general characteristics of persistent pollutants. The first two are DDT and PCBs, both chlorinated hydrocarbons, one from agriculture the other from industry. The third concerns mercury compounds.

DDT residues can now be found in most animal tissues. A specific instance in California is the universal occurrence of DDT and metabolites in frogs from the Sierra Nevada, most areas of which have not been treated with DDT in insect control,[16] Both vertical and latitudinal gradients of p,p′DDE (the commonest DDT metabolite) in the fat bodies of frogs show the relationship to primary sites of application. Values range from an average of 1.32 ppm in the northern range to 5.38 ppm in the Yosemite-Sonora region adjacent to the San Joaquin Valley. Lower elevations (below 5000 feet) have tissue levels averaging 3.46 ppm, not significantly different from those above 5000 feet (aver. 3.19 ppm) on the western face of the mountains. Apparently DDT residues are carried eastward from the Central Valley to produce in frogs ultimate concentrations related to precipitation patterns. Of several hundred frogs examined throughout the Sierra Nevada, all contained some DDE. The important points to make here are that: residues were carried a great distance in air; they were removed from air by precipitation; they were picked up, stored and transferred in animal food chains; and they were universal contaminants. Many millions of pounds of DDT have been used in California since its advent in 1945. The amount still environmentally impounded must truly be awesome.

In a totally different area—but one also typifying an area where DDT was never applied—the blubber of gray and sperm whales was analyzed for DDT and metabolites.[17] Specimens taken off the California coast averaged 0.36 ppm in the blubber of gray whales and 6.0 ppm in sperm whales. The 16-fold greater values in sperm whales than in gray whales is explained by the food habits of the two species. The sperm whale eats large organisms, higher up the food chain. To the dimension of physical dispersal of metabolites must now be added specific differences between organisms in the ability to concentrate residues in tissues.

The chemically related PCBs are the products of industry but their dispersal and concentration patterns strongly parallel those of the insecticides. Concentrations of PCB in fish and birds are highest in such outfalls as San Francisco Bay and San Diego Bay, and concentration gradients apparently exist from these areas to regions more remote.[2,4,7] PCB has been shown to be a powerful inducer of steroid hydroxylases in birds,[2,18] and, with p,p'DDE, may therefore be partially responsible for the aberrant calcium physiology observed in species of raptorial and fish-eating birds that accumulate chlorinated hydrocarbons. It is probable that PCB in human food supplies would induce the synthesis of comparable enzymes in man. Yet the toxicity of PCBs whether acute or subtle is still a subject for experiment.

The toxicity of mercury has been known since ancient times. New upon the scene are the organomercurials and their ecologic distributions. Organic mercury has become widely used in industry and agriculture. The chief sources of environmental contamination are methylated mercury used in the production of chlorine and caustic soda, phenyl mercuric acetate (PMA) used in slime control in the pulp industry, and PMA and other alkyl mercury compounds used as fungicides on seed.

The best know instance of environmental pollution leading to human death occurred in Japan.[11,19] An industrial plant employing methyl mercury chloride in the production of acetaldehyde produced effluents contaminating fish and shellfish at lethal levels in Minamata Bay. Forty-one deaths resulted. Also detected were congenital neurological injuries indicating that ingested mercury penetrates the placental barrier. Cats and rats in the city were also affected. Fish samples normally contained above 0.5 ppm mercury. Daily consumption of fish contaminated at 5.0 ppm was judged to induce lethality.[20]

Sweden has voiced similar alarms.[11] Widespread contamination of fish and birds led to stringent industrial controls in 1966 and abolition of seed dressings containing alkyl mercury. Sweden still allows a 1.0 ppm mercury contamination level in edible fish, judged by many to be much too high.

Confirmation of the relatively recent nature of environmental contamination by mercury is provided by a Swedish paper[21] describing mercury content in the feathers of 11 species of birds in museums collected over a century's time. In all species, mercury content was roughly constant in the period 1840-1940. Beginning in the 1940's mercury content increased 10 to 20 fold. Highest levels were in fish-eating birds, lowest in seed-eaters.

Recent publicity has been accorded above-tolerance (0.5 ppm) levels in fish and birds in many areas of the United States and Canada. In California particularly the problem is complicated by geologic deposits of mercury and the inestimable but unquestionably large amounts of metallic mercury released into streams by gold recovery processes.

Almost all mercury identified in animal tissue is methylated. Mercury compounds such as PMA are rather quickly reduced in nature to inorganic mercury. Recently it has been shown,[22] however, that bacteria in anaerobic ecosystems convert inorganic mercury to methyl mercury. This latter form is unfortunately both highly toxic and stable. Only regulation of the sources of contamination therefore can control accompanying environmental hazard.

Biological Magnification of Persistent Pollutants

Pollutants with the necessary characteristics earlier identified become hazardous because of two kinds of biological magnification. One group of animals referred to as environmental concentrators is capable of acquiring high concentrations of pollutants in short order. In general they are filter-feeding organisms such as shellfish. The simple fact of ubiquitous predation—that one animal eats another—produces the second type of biological magnification. This is normally referred to as food-chain concentration. As illustrated earlier, flesh-eating organisms such as fishes and raptorial birds contain the highest residue loads to be found in nature. Such concentrations are not unexpected considering their position in the food chain. Man is, of course, a terminal consumer in the food chain; hence the need for particular caution in regulating contaminant levels.

Food-chain or trophic concentration should be our chief concern. Magnification of residues may occur by three methods. (What follows applies mainly to persistent organochlorine residues.)

Physiological concentration occurs when residues are stored and accumulated by particular tissues within the bodies of individual organisms. A near straight-line relationship exists between lipid fractions of a tissue and the amounts of residues contained. For this reason the milk of mammals and the sexual organs of animals—both with high lipid fractions—show the highest capability for concentrating residues.

Biological concentration occurs in those instances in which residues are picked up through the skin or respiratory surfaces. This method is common in aquatic environments.

Trophic concentration (through food-chains) occurs simply because one organism depends on another for food. Physiologically stored residues accompany foods eaten, are assimilated and stored in the predator which in turn, if eaten, passes along larger amounts of residues. All three methods of concentration lead to magnified quantities of residues in secondary consumers in food-chains.

Hazard to Man and Animals

For this discussion I have deliberately exempted accidental, occupational and suicidal contact with toxic materials. Many hundreds of case histories have been recorded by the World Health Organization, and in California public health officials are particularly sensitive to the many problems connected with agricultural uses of poisons.

DDT (sometimes traces of dieldrin) occurs in human fat in the United States on an average of 12 ppm.[15] DDT regularly occurs in mother's milk in trace amounts and sometimes in much higher concentration. Since no residues are allowable in commercial milk products, some human milk clearly violates legal standards for use. Residues in human foods derive either from a fraction remaining on foods from the original application or in animal products from the results of physiological concentration.

The significance of these residues is hotly debated. Most of us would prefer not to have any residues at all, thereby obviating the question of harmful effects. Recent autopsy studies hint at a strong correlation between residue levels and liver cancers.[15] Yet, on balance, there seem to be no general effects from the presence of residues. Regulatory control of residues in human foodsuffs in the United States is now relatively efficient. Still, the warnings given by wild species should dictate long-term study on human beings.

Residue levels in the foodsuffs of wild species is obviously not regulated by law (except in indirect ways) and they show directly the results of all three manners of residue concentration. Acute mortality from chemicals (for example, "fish-kills") is common in wild species and many thousands of analyses establish the occurrence of residues of many kinds in wild species. These effects are important but in the long run are neither as insidious nor as potentially disastrous as those affecting the reproduction of wild species. Some examples of this kind are localized, such as the killing of trout fry in Lake George, New York, due to accumulated pesticide residues in eggs. These local effects are correctible in time. The same cannot be said for species-wide effects in which reproductive inhibition due to pesticide residue accumulation in adults and eggs is apparently responsible for significant declines in numbers. Regional extinction of some species has already been the result.

Ten families of birds—chiefly raptorial and fish-eating species—have already been implicated in such declines. The best known example is the peregrine falcon that began its decline in Europe and North America coincident with the introduction of DDT.[23] This bird has already become extinct throughout most of its range in the United States since 1950. Young birds simply cannot survive. But an important observation is that adult behavior is also altered. Birds lay smaller eggs with thinner shells; they eat their own eggs; they break many. All these effects suggest calcium deprivation.[5,18] Current theory suggests inordinate destruction of circulating estrogens, necessary for the provision of calcium for eggshells.[2,24,25] Reproductive failure is assured by this means.

The same pattern seems to be occurring in the widely publicized reproductive failures of brown pelicans on the Channel Islands off California. In 1970, for example, one breeding colony of 552 pairs of pelicans on Anacapa Island produced only one surviving young (F. Gress, personal communication). Eggshells of these birds are soft and rubbery, resembling reptilian eggs. Pesticide residues (as well as lead) in adult birds range into hundreds of ppm.

A doctoral student of mine, currently (August 1970) in Guatemala, reports collecting 50 aberrant eggs from a cattle egret colony. All had "spongy" eggshells. Enzymatic destruction of estrogens induced by pesticide residues clearly is not a provincial matter.

A Concluding Commentary

Many of the persistent waste products of technogolical man now contaminate the earth's ecosystems. Their presence need not necessarily be construed as hazardous, but the fact of their occurrence is reason enough for serious environmental concern. Beyond that, I have demonstrated in text two other characteristics that should instill yet more concern. Persistent residues are at once now uncontrollable and unpredictable. There is no known way to remove the residues of pesticides, mercury, lead and other chemicals from the environment. Historically we have depended on dilution and degradation to minimize the effects of contaminants. Such dependence can only be partially successful. Mobility and stability of chemicals combined with biological concentration ensure that the historical dependence is no longer applicable. We can depend on regulatory actions to minimize environmental input. These actions take many forms, familiar to us all. Limitation of chlorinated hydrocarbon insecticides, elimination of lead from gasoline, restricting industrial effluents, and establishing monitoring systems are examples. Whether or not comforting, my personal view is that these actions have come too late. The millions of pounds of DDT, mercury and lead now circulating in biological systems will plague us for decades to come even if all such inputs were withdrawn immediately. Of such withdrawal there is scant likelihood. For example, the "enlightened" view regarding DDT usage is to restrict its application in the United States but not to restrict the export trade. My earlier description of the global mobility of persistent residues should indicate the proper course of action.

Unpredictability is more frightening in some ways than uncontrollability. Technological man is unconsciously conducting global empirical experiments without full regard for their consequences. A peregrine falcon or a brown pelican may not in themselves be important to many human beings. But they along with hundreds of other wild species have already demonstrated the precarious balance that technological man strikes with the living substance of the earth. Does residual p,p'DDE, for example, have the same capacity to upset hormonal balances in man as has been already demonstrated in several species of birds and mammals? When may we expect continually increasing residual levels of all persistent residues to influence man on a broad scale. Our "incidents" now are viewed as focal necroses. I view them as discovered examples of much more widely occurring phenomena. We are unfortunately in the position of not even knowing what has already happened.

Under President Kennedy, a report was issued entitled "Restoring the Quality of Our Environment." The key words are "restoring" and "quality." These mean that we wish to put back something that sustains us both productively and esthetically. This view is not an atavistic notion that we wish things were as simple as they used to be. We may have indeed lost a great deal that we value. But what we really need to reestablish is a working control system. At this time, it seems to me that our relation to environment is dangerously imbalanced and out of control.

REFERENCES

1. Acree F, Beroza M, Bowman MC: Codistillation of DDT with water. Agri Food Chem 11:278, 1963
2. Risebrough RW, Reiche P, Peakall D, et al: Polychlorinated biphenyls in the global system. Nature 220:1098, 1968
3. Bailey TE, Hannum JR: Distribution of pesticides in California. J Sani Eng Div, Am Soc Civil Eng, Proc 5510:27, 1967
4. Risebrough RW: Chlorinated hydrocarbons in marine ecosystems, Chap 7, *In* Miller MW, Berg GC (Eds): Chemical Fallout. Springfield, CC Thomas, 1969, pp 5-23
5. Wurster CE, Wingate D: DDT residues and declining population in the Bermuda petrel. Sci 159:979, 1968.
6. Cohen J, Pinkerton C: Widespread translocation of pesticides by air transport and rain-out. *In* Organic pesticides in the environment. Am Chem Soc, Adv in Chem 60:163, 1966
7. Risebrough RW, Huggett RJ, Griffin JJ, et al: Pesticides: Transatlantic movements in the northeast trades. Sci 159-1233, 1968
8. Keith JO, Hunt EG: Levels of insecticides in fish and wildlife. Trans 31st N Am Wildl Conf: 150, 1966
9. Peterle T: DDT in antarctic snow. Nature 224:620, 1969
10. Johnson DW: Pesticides and fishes—A review of selected literature. Trans Am Fish Soc, 97:398, 1968
11. Miller MW, Berg GC (Eds): Chemical Fallout. Springfield, CC Thomas, 1969
12. Moore NW: A synopsis of the pesticide problem. Adv in Ecol Res 4:75, 1967
13. Robinson J: Persistent pesticides. Amer Rev Pharm 10:353, 1970
14. Rudd RL: Pesticides and the living landscape. Madison, U Wisc Press, 1964
15. US Dept Health, Education, and Welfare: Report of the Secretary's Commission on Pesticides and Their Relationship to Environmental Health. GPO, 1969
16. Cory L, Fjeld F, Serat W: Distribution patterns of DDT residues in the Sierra Nevada mountains. Pesticides Monitoring J 3:204, 1970
17. Wolman AA, Wilson AJ: Occurrence of pesticides in whales. Pesticides Monitoring J 4:8, 1970
18. Peakall DB: Pesticides and the reproduction of birds. Sci Amer 222:72, 1970
19. Kurland RF, Faro SM, Siedler H: Minamata disease. World Neurol 1:360, 1960
20. Birke G, Johnels A, Plantin LO, et al: Metylqvick-Silverförgifning genom fortäring av fisk Svenska Läkartidü, 64:3628, 1967
21. Berg W, Johnels A, Sjöstrand B, et al: Mercury contents in feathers of Swedish birds for the past 100 years. Oikos 17:71, 1966
22. Wood JM, Kennedy FS, Rosen CG: Synthesis of methylmercury compounds by extracts of a methanoganic bacterium. Nature 220:174, 1968
23. Hickey JJ: Peregrine falcon populations—Their biology and decline. Madison, U Wisc Press, 1969
24. Hickey JJ, Anderson DW: Chlorinated hydrocarbons and eggshell changes in raptorial and fish-eating birds. Sci, 162-271, 1968
25. Porter RD, Wiemeyer SN: Dieldrin and DDT: Effects on sparrow hawk eggshells and reproduction. Sci 165:199, 1969

TREATING PESTICIDE POISONING

"With the increasing use of strong agricultural pesticides, acute organophosphate poisoning is now more widespread than medical knowledge of its diagnosis and treatment. The condition is misdiagnosed as any number of clinical entities, including acute infection of the nervous system and cerebrovascular disease. . . .

"Emergency treatment of a recognized organophosphate poisoning of a severe nature cannot await laboratory confirmation. Artificial respiration, preferably with a respirator; atropine sulfate, 2 to 4 mg intravenously at five- to ten-minute intervals until atropinization occurs, and maintained for 24 to 48 hours or more; 2-PAM intravenously in doses commensurate with body weight; and decontamination of the stomach, skin, hair, nails and eyes are measures to be instituted immediately."

—WALTER F. EDMUNDSON, M.D., Miami
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